

Time-resolved *in Situ* Powder Diffraction Studies of Oil Well Cement Hydration at Elevated Temperatures

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Introduction

Cement is very important to the oil well drilling industry because it is used as a “grout” for wellbore liners, making the well gas-tight and mechanically stable. Cement slurry is pumped into the gap between the liner and the surrounding rock. The grouting process may fail if the slurry begins to set before the pumping is completed, and such failures are generally costly, so good control of the setting times under wellbore conditions is highly desirable. Well drilling to depths of 30,000 feet or more has become fairly common practice [1], and significantly elevated temperatures are encountered at such depths. To offset the accelerating effects of the elevated temperatures, set-retardant admixtures are added to the cement. The present work examines the mode of action for some of these admixtures by using time-resolved powder diffraction on cements hydrating at 66, 93, 121, and 177°C.

The cement used for oil well grouting closely resembles the ordinary Portland cement used in construction; the main difference is that it has a higher Fe/Al ratio in its elemental composition. The main phases in unhydrated oil well (Class G or Class H) cement are tricalcium silicate Ca_3SiO_5 (about 50%), dicalcium silicate Ca_2SiO_4 (about 30%), calcium aluminoferrite $\text{Ca}_2\text{FeAlO}_5$ (about 15%), and calcium sulfate (2-3%, usually as the dihydrate gypsum). When the conventional cement chemistry abbreviations of C = CaO, S = SiO_2 , A = Al_2O_3 , and F = Fe_2O_3 are used, the first three of these may be written as C_3S , C_2S , and C_4AF , respectively. At ambient temperature, the most important cement hydration process is the conversion of the silicate phases to $\text{Ca}(\text{OH})_2$ (or CH, where H = H_2O) and an amorphous calcium silicate hydrate generally referred to as C-S-H. At sufficiently high temperatures, the crystalline calcium silicate hydrates C_2SH and $\text{C}_6\text{S}_2\text{H}_3$ (also known as jaffeite) form. The resulting cement matrix has lower mechanical strength and higher permeability, although this result is not necessarily a serious drawback [2]. The most rapid reaction during the early hours of cement hydration at ambient temperature is the formation of ettringite, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$. Above about 80°C, this decomposes to yield 14-water monosulfate, $\text{Ca}_4\text{Al}_2\text{O}_6(\text{SO}_4)\cdot 14\text{H}_2\text{O}$. This itself is unstable at higher temperatures.

Methods and Materials

Time-resolved powder diffraction data were collected at DND-CAT beamline station 5-BM-D by using a Debye-Scherrer geometry. A 65-keV beam, collimated to 1×1 mm, was used for the measurements. The high photon energy was chosen to provide adequate penetration of the sample cell. Diffraction patterns were measured by using a Mar 165 charge-coupled device (CCD) detector, placed ~175 cm from the sample. With this arrangement, complete Debye-Scherrer rings could be measured up to about $5^\circ 2\theta$, corresponding to a minimum d spacing of about 2.2 Å. The raw diffraction data were converted to 2θ /intensity by using the program FIT2D [3], with 2θ values assigned based on a TiO_2 diffraction standard calibration. During experimental runs, a diffraction pattern was recorded every 5 minutes over time periods of between 3 and 12 hours. This allowed us to follow the hydration of the cement paste in real time.

The cement slurry was contained in PEEK-lined titanium “cans” sealed with Swagelock fittings. The cans were made from 3/8-in. titanium rod bored out to a 1/4-in. internal diameter. The wall thickness was reduced to 0.01 in. in the area where the x-ray beam entered and exited. A small fan oven was designed and built specifically for the experiments. The sample cans were mounted in the middle of the oven to provide a clear x-ray beam path with Kapton® entry and exit windows. During a typical experiment, the oven was ramped to the final temperature over a period of 54 minutes, and this temperature was then maintained until completion of the measurements. The oven temperature was logged automatically every 30 seconds during data collection.

Results

Many runs were performed by using different admixtures and temperatures. This body of data is very informative, but space precludes a complete presentation. An example data set is shown in Fig. 1 to illustrate the wealth of information that was obtained; diffraction peaks of particular interest are labeled. The sample for this run contained a retardant admixture and was ramped from room temperature to 121°C (250°F) during the first 54 minutes.

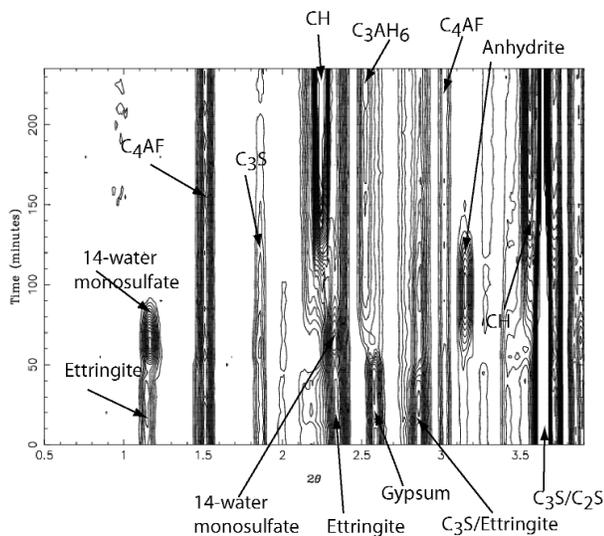


Fig. 1. Time-resolved diffraction data for a retarded type H cement slurry hydrating at 121°C.

Salient features in these data include the following: (1) C_3S and C_2S are depleted over time, and from about 110 minutes onward, CH is precipitated. (2) Ettringite forms early, but then decomposes to yield 14-water monosulfate after about 40 minutes. (3) At about 60 minutes, gypsum transforms to anhydrous calcium sulfate, or “anhydrite.” (4) From about 70 minutes onward, C_3AH_6 is formed.

From data acquired under many different conditions, the hydration mechanisms and kinetics seen in the different runs can be compared. Figure 2 shows beam-normalized C_3S peak intensities versus time, from a series of samples that were hydrated at 93°C in the presence of different retarders. The various effects of the retarders on the rate of C_3S depletion are clearly discernible. Typically, hydration of the C_3S initially proceeds slowly, pauses, and then rapidly accelerates. The time at which the rapid acceleration occurs depends on the retarder/retarder concentration that is employed.

Discussion

In situ x-ray powder diffraction at elevated temperatures has enabled us to follow the hydration of oil well cement slurries in detail and establish the influence of different retardant admixtures. The use of high-energy x-rays allowed us to perform the measurements under autogenous pressure in titanium sample “cans” and thus prevent the loss of water. The diffraction data not only show the hydration behavior of the calcium silicate phases but also provide information

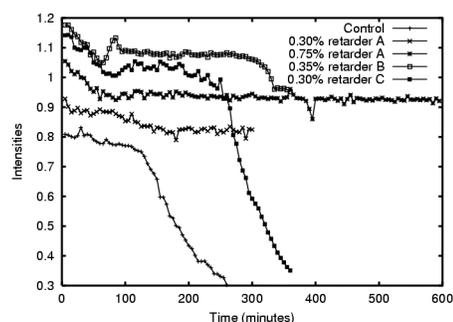


Fig. 2. C_3S peak intensities versus time for samples containing different retarders and retarder concentrations. The final run temperature was 93°C in each case. Retarder A is a synthetic copolymer, retarder B is hydroxycarboxylic acid, and retarder C is a modified natural polymer.

about the stabilities of sulfate-bearing phases. These experiments have uncovered an unanticipated crystalline intermediate on the hydration pathway; suggested, in general terms, a mechanism for retarder action; and hinted at a link between cement chemistry, as seen by diffraction, and cement slurry rheology.

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